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# PHOTOLUMINESCENCE FROM PRESSURE - ANNEALED NANOSTRUCTURED SILICON DIOXIDE AND NITRIDE FILMS

A. MISIUK<sup>a</sup>, L. REBOHLE<sup>b</sup>, A. ILLER<sup>c</sup>, I. E. TYSCHENKO<sup>d</sup>, J. JUN<sup>e</sup> and A. PANAS<sup>a</sup>

(a) Institute of Electron Technology, Al. Lotnikow 46, 02-668 Warsaw, Poland; (b) Institut für Ionenstrahlphysik und Materialforschung, Dresden, POB 510119 Dresden, Germany; (c) Institute of Vacuum Technology, Dluga 44/50, 00-241 Warsaw, Poland; (e) Institute of Semiconductor Physics RAS, 630090 Novosibirsk, Russia; (d) High Pressure Research Centre, Sokolowska 29/37, 01-142 Warsaw, Poland

#### Abstract

Light emission in thin films (SiO<sub>2</sub>, SiO<sub>2</sub>:Si and Si<sub>3</sub>N<sub>4</sub>) on a single crystalline silicon surface has been investigated after treatment at enhanced argon pressure, HP. Pronounced effect of HP up to 1.5 GPa during annealing up to 1550 K on photoluminescence, PL, of the SiO<sub>2</sub>, SiO<sub>2</sub>:Si and Si<sub>3</sub>N<sub>4</sub> films of 0.1 - 1.2  $\mu$ m thickness has been stated. The pressure - temperature treatment results in development and enhancement of ultraviolet and visible PL at about 290 - 320, 360, 460, 600 and 680 nm, related to stress induced creation of PL active silicon nanoclusters and other oxygen deficient defects.

#### 1. Introduction

Nanocrystalline materials have been attracting rapidly increasing interest in the last decade in the areas of magnetics, catalysts, mechanics and optoelectronics. The last is related, among others, to the hopes of obtaining visible light emission from silicon or silicon - related materials. Light emission from SiO<sub>2</sub>, SiO<sub>2</sub> implanted by Si (SiO<sub>2</sub>:Si) or Ge, Si<sub>3</sub>N<sub>4</sub> and from porous silicon, pSi, has been intensively investigated because of their usefulness in silicon based optoelectronics. Silicon based optoelectronics refers to the integration of photonic and electronic components on a Si chip or wafer. The photonics adds value to the electronics, and the electronics offers low cost mass production benefits [1].

Bulk silicon (with bandgap value E = 1.12 eV) is an indirect bandgap semiconductor, and so phonons must assist in radiative electron hole recombination. It results in the low photoluminescence, PL, efficiency, of the order of ~10<sup>-5</sup> which can be increased in the case of a dislocation - free crystal with perfectly passivated surface [2].

Efficient room temperature PL at about 1.8 eV from pSi prepared by electrochemical etching of single crystalline Si has been reported. However, PL from pSi degrades in ambient conditions; moreover, pSi is fragile and of very poor thermal conductivity so, in spite of enormous efforts, it is still far from being introduced into wide use.

There are two general explanations of visible PL from pSi. One mechanism is related to the presence of some PL active surface contaminants; the other one is related to a quantum - size effect. In nanometer sized Si crystal the effective mass approximation predicts bandgap upshift for  $\Delta E \sim d^2$  where d is the nanocrystal diameter [2]. This second effect suggests possible usefulness of other materials containing semiconductor nanocrystals, e.g. Si, (C, Ge,..), dispersed in optically transparent film (e.g. SiO<sub>2</sub>). Such materials can be produced by ion implantation with subsequent annealing.

As it has been stated [3, 4], enhanced pressure of ambient gas at annealing (HT - HP treatment) of oxygen containing Czochralski grown silicon, Cz-Si, and of Si - Ge solid solution exerts pronounced effect on oxygen and germanium diffusivity, clustering etc. It inspired our recent investigations of the HT - HP treatment effect on visible PL from silicon dioxide implanted by silicon, SiO<sub>2</sub>:Si [5, 6].

Effects of the HT - HP treatment on creation of silicon nanoclusters, and on PL from the SiO<sub>2</sub>, SiO<sub>2</sub>:Si and Si<sub>3</sub>N<sub>4</sub> thin films grown (deposited) on single crystalline silicon are reported in this paper.

### 2. Experimental

Silicon dioxide,  $SiO_2$  films of 0.1 - 1.2 µm thickness on n - and p - type (001) oriented single crystalline Czochralski grown, Cz-Si, wafers were prepared by oxidation in dry oxygen at up to 1420 K, oxidation in the  $O_2 + N_2$  mixture at 1370 K, oxidation in the  $O_2 + H_2$  ("wet oxygen") atmosphere at 1270 - 1370 K or by low pressure chemical vapour deposition, LPCVD, at 670 - 920 K from the gas containing silicomethane and oxygen, typically with the final densification at 1270 K.

Some 500 nm thick  $SiO_2$  films were implanted with  $Si^+$  ions at an energy of 100 keV and then at 200 keV using respective doses of  $1.2 \times 10^{16}$  cm<sup>-2</sup> and  $2.0 \times 10^{16}$  cm<sup>-2</sup> (low dose, LD, total dose  $3.2 \times 10^{16}$  cm<sup>-2</sup>), of  $2.3 \times 10^{16}$  cm<sup>-2</sup> +  $4.4 \times 10^{16}$  cm<sup>-2</sup> (high dose, HD, total dose  $6.7 \times 10^{16}$  cm<sup>-2</sup>) and of  $3.9 \times 10^{16}$  cm<sup>-2</sup> +  $6.3 \times 10^{16}$  cm<sup>-2</sup> (very high dose, VHD, total dose  $1.02 \times 10^{17}$  cm<sup>-2</sup>). In what follows such silicon implanted films are referred to as the  $SiO_2$ : Si films.

Silicon nitride,  $Si_3N_4$ , films of 0.12  $\mu m$  thickness on the Cz-Si surface were prepared by LPCVD from the silicomethane - ammonia mixture at 920 K.

The  $SiO_2/Si$ ,  $SiO_2:Si/Si$  and  $Si_3N_4/Si$  samples were subjected to anneals for up to 10 h up to 1550 K under enhanced (up to 1.5 GPa) hydrostatic argon pressure, HP [4, 5].

PL peaks observed at particular excitation wavelength were often accompanied by scattered radiation. To avoid possible mistakes with interpretation of the obtained results, different excitation sources were applied.

PL of the HT - HP treated SiO<sub>2</sub>, SiO<sub>2</sub>:Si and Si<sub>3</sub>N<sub>4</sub> films was excited at room temperature, RT, by ultraviolet lamp ( $\lambda_{ex}$  = 240 - 250 nm), He - Cd laser ( $\lambda_{ex}$  = 325 nm) or Ar laser ( $\lambda_{ex}$  = 488 nm) and recorded employing a Spex Fluoromax spectrometer and R 928 Hammatsu photomultiplier (for measurements using  $\lambda_{ex}$  = 240 - 250 nm) or a photomultiplier with S11 cathode (for other excitations).

#### 3. Results

### 3. 1 PHOTOLUMINESCENCE FROM PRESSURE ANNEALED SILICON DIOXIDE FILMS

As deposited thermally grown  $SiO_2$  films excited by  $\lambda_{ex} = 250$  nm indicate at RT very weak PL at about 460 nm [5].

PL spectra from the 290 nm thick  $SiO_2$  films obtained at RT using 240 nm excitation wavelength are presented in Fig. 1 for the samples treated at different HT - HP conditions and in Fig. 2 - for the samples treated at 1470 K - HP. PL spectrum for the sample treated at 1550 K - 1.5 GPa - 10' is presented for comparison.

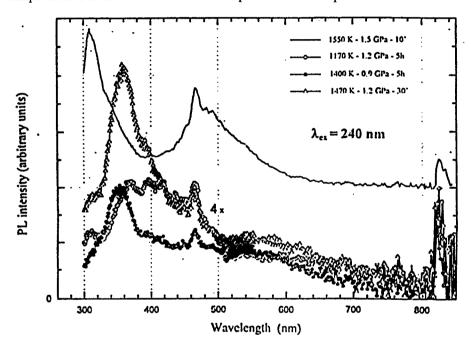


Figure 1. PL spectra from thermally grown ( $O_2 + H_2$ , 1470 K) silicon dioxide films of 290 nm thickness, subjected to HT - HP treatments at different temperatures - pressures: 1170 K - 1.2 GPa - 5 h, 1400 K - 0.9 GPa - 5 h, 1470 K - 1.2 GPa - 30° and 1550 K - 1.5 GPa - 10°. PL excitation wavelength  $\lambda = 240$  nm.

Minor PL measured for the samples treated at 1170 K - 1.2 GPa - 5 h (Fig. 1) and at 1470 K - 1.5 GPa - 10' (Fig. 2) is mostly due to scattering of exciting ( $\lambda_{ex}$  = 240 nm) radiation. This seems to be also the case for the sharp PL peaks at 465 nm and 820 nm observed for almost all samples. However, as it follows from the PL results obtained using the 325 nm excitation, this scattered radiation can be superimposed on the wide "real" weak PL peak at 520 - 560 nm (at least for the sample treated at 1550 K - 1.5 GPa - 10', see also Figs 3 and 4).

Comparatively strong PL peaks at 290 - 320 nm and at 340 - 380 nm were observed for the samples treated at 1400 - 1470 K - 0.9 - 1.5 GPa for above 30' (Fig 1, 2).

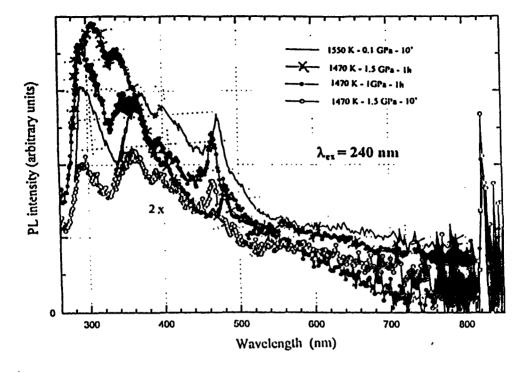


Figure 2. PL spectra from thermally grown (O<sub>2</sub> + H<sub>2</sub>, 1470 K) silicon dioxide films of 290 nm thickness, subjected to HT - HP treatments at 1470 K and at 1550 K: 1470 K - 1 GPa - 1 h, 1470 K - 1.5 GPa - 10', 1470 K - 1.5 GPa - 1 h and at 1550 K - 0.1 GPa - 10'. PL excitation wavelength  $\lambda$  = 240 nm.

Similar HT - HP induced PL (but peaking at 305 nm) was detected for the sample treated at 1550 K - 1.5GPa for 10' (Fig. 1) whereas the sample treated at the same conditions but under 0.1 GPa indicated PL similar to that detected for the samples treated at 1470 K (Fig. 2).

As it follows from measurements with the 325 nm excitation, the prolonged (1-5h) HT - HP treatment at  $\geq 1170$  K - 1.2 - 1.5 GPa of thermally grown  $SiO_2$  results in a wide PL band at 400 - 600 nm (Figs 3, 4). Intensity of the 400 - 600 nm PL band from the thermally grown  $SiO_2$  of 290 nm thickness (Fig. 3) was dependent on conditions of the HT - HP treatment (temperature, pressure, time) and was of the highest value for the samples HP - treated at 1400 - 1470 K for 1 - 5 h. The short time treatments (10' - 30') at 1270 - 1470 K - 0.1 - 1.5 GPa resulted in very weak PL at this wavelength range. The same concerned the samples HT - HP treated at below 1170 K.

The PL intensity from the  $SiO_2/Si$  samples treated at 1400 K - 1.2 GPa for 5 h was dependent on the preparation method. It was comparatively strong for the thin  $SiO_2$  films prepared by oxidation of Si in a dry oxygen atmosphere (Fig. 4, spectrum d) but much weaker for the case of  $SiO_2$  films prepared by oxidation of silicon in the  $(O_2 + N_2)$  or  $(O_2 + H_2)$  gas mixtures (Fig. 4, spectra a - c).

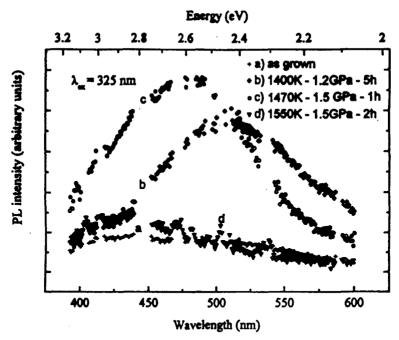


Figure 3. PL spectra from thermally grown ( $O_2 + H_2$ , 1470 K) 290 nm thick  $SiO_2$  films, as grown and subjected to HT - HP treatments at 1400 K - 1.2 GPa - 5 h, 1470 K - 1.5 GPa - 1 h and at 1550 K - 1.5 GPa - 2 h.

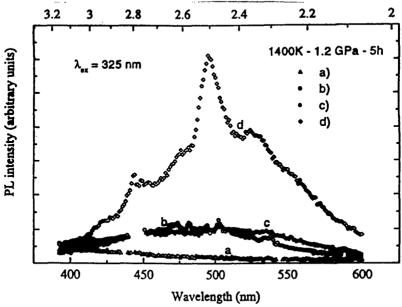


Figure 4. PL spectra from silicon dioxide films treated at 1400 K - 1.2 GPa for 5 h. SiO<sub>2</sub> films were thermally grown at different conditions: a)  $(O_2 + N_2)$  mixture, 1370 K, 260 nm thick; b) wet oxygen  $(O_2 + H_2)$ , 1470 K, 290 nm thick; c) wet oxygen  $(O_2 + H_2)$ , 1270 K, 470 nm thick; d) dry oxygen, 1370 K, 260 nm thick.

### 3. 2 PHOTOLUMINESCENCE FROM SILICON IMPLANTED PRESSURE ANNEALED SILICON DIOXIDE FILMS

The PL spectra from thermally grown  $0.5 \,\mu m$  thick  $SiO_2: Si / Si$  films (2 stage VHD implantation,  $Si^+$  energy of  $100 \, keV$ ,  $3.9 \times 10^{16} \, cm^{-2} \, dose + Si^+$  energy of  $200 \, keV$ ,  $6.3 \times 10^{16} \, cm^{-2} \, dose$ ) as implanted and subjected to the post implantation HT - HP treatment at 720 K, are presented in Fig. 5.

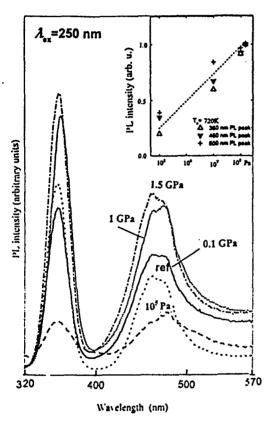


Figure 5. PL spectra (at 300 K) from thermally grown 0.5  $\mu$ m thick SiO<sub>2</sub> films VHD implanted with silicon, as implanted (ref) and treated at 720 K - (10<sup>5</sup>Pa - 1.5GPa) for 10 h. Insert: dependence of the PL intensity peaks at 360, 460 and 600 nm on HP during annealing at 720 K for 10 h. PL excitation wavelength  $\lambda$  = 250 nm.

The as implanted sample exhibits two PL peaks in the short wavelength range at about 360 nm (ultraviolet) and 460 nm (blue). The PL peaks at 360, 460 and 600 nm (the last not seen in Fig. 5) were detected for the HT - HP treated samples. The peak ntensity increased (see insert) with HP.

Effect of the HT - HP treatment at 1400 K on the PL spectra from thermally grown 0.5  $\mu$ m thick silicon implanted SiO<sub>2</sub> films (2 stage implantation, low and high oxygen doses) is presented in Fig. 6 for PL excitation wavelength  $\lambda$  = 250 nm. The intensity of the short wavelength photoluminescence at 360 nm was strong for the HD implanted samples treated at 1400 K - 1.2 GPa for 5 h, while during annealing at ambient pressure (10<sup>5</sup> Pa) this peak reached a maximum for the samples annealed at about 770 K.

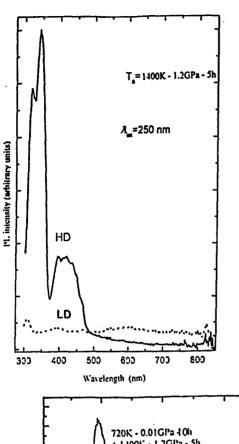


Figure 6. PL spectra (at 300 K) from thermally grown 0.5  $\mu m$  thick SiO<sub>2</sub> films implanted with low and high silicon doses, LD and HD, treated at 1400K - 1.2 GPa for 5 h. PL excitation wavelength  $\lambda = 250$  nm.

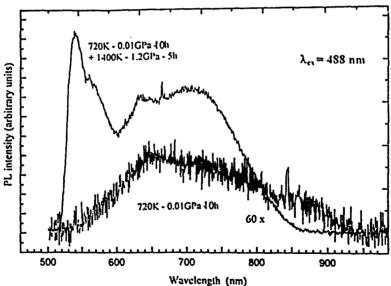


Figure 7. PL spectra from thermally grown 0.5  $\mu$ m thick VHD SiO<sub>2</sub>:Si/Si samples subjected to treatment at 720 K - 0.01 GPa and additionally at 1400 K - 1.5 GPa. PL spectrum of the sample treated at 720 K - 0.01 GPa was magnified (60 times). PL excitation wavelength  $\lambda$  = 488 nm.

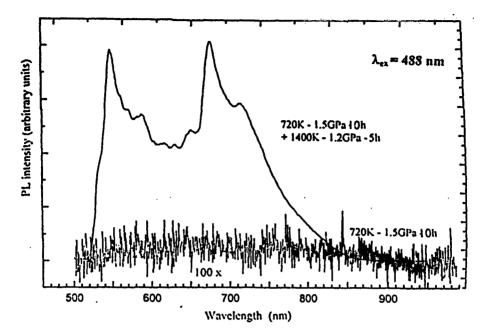


Figure 8. PL spectra from thermally grown VHD 0.5  $\mu$ m thick SiO<sub>2</sub>: Si films treated at 720 K - 1.5 GPa and additionally at 1400 K - 1.2 GPa. PL spectrum of the sample treated at 720 K - 1.5 GPa was magnified (100 times). PL excitation wavelength  $\lambda$  = 488 nm.

The effect of HT - HP treatment at 720 K and at 1400 K on PL spectra from thermally grown 0.5  $\mu$ m thick VHD SiO<sub>2</sub>: Si films is presented in Figs 7 and 8 for PL excitation wavelength  $\lambda = 488$  nm. The higher - energy PL peak at 550 nm is related probably to scattered radiation whereas that at 660 - 750 nm corresponds to the "real" PL. Enhanced pressure during sample annealing at 720 K leads to practically complete quenching of PL at 660 - 750 nm whereas additional treatment at 1.2 GPa resulted in PL peaking at about 680 nm, being dependent on conditions of the treatment.

### 3. 3 PHOTOLUMINESCENCE FROM PRESSURE ANNEALED SILICON NITRIDE FILMS

The effect of the HT - HP treatment on PL from silicon nitride (Figs 9 - 11) was investigated for  $Si_3N_4$  films of 0.12  $\mu m$  thickness deposited at 920 K on the Cz-Si surface by LPCVD method from the silicomethane - ammonia mixture. PL at 380 and 520 nm [7] (excited by ultraviolet lamp,  $\lambda_{ex}$  = 350 nm) has been reported for the silicon nitride films deposited at 1060 K by LPCVD method from the NH $_3$  - SiH $_2$ Cl $_2$  mixture. The HT - HP treatment of the Si $_3N_4$ /Si samples resulted in PL (excitation by ultraviolet lamp,  $\lambda_{ex}$  = 240 nm or He - Cd laser,  $\lambda_{ex}$  = 325 nm) peaking at about 290, 360 and 450 nm.

The  $Si_3N_4$  / Si sample treated at 1550 K - 0.1 GPa - 10' indicates PL at 290 and 360 nm (the sharp peak at 460 nm can be related to scattered excitation light).

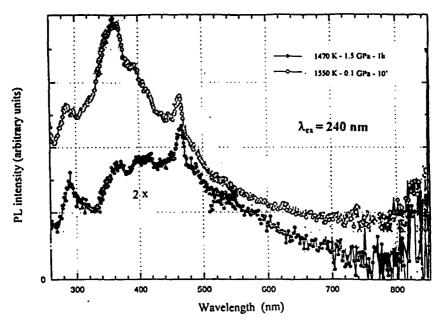


Figure 9. PL spectra from 120 nm thick  $Si_3N_4$ / Si samples ( $Si_3N_4$  deposited at 920 K by LPCVD method from silane -  $NH_3$  mixture) after subjecting to HT - HP treatments at 1470 K - 1.5 GPa for 1 h and at 1550 K - 0.1 GPa for 10'. PL excitation wavelength  $\lambda = 240$  nm.

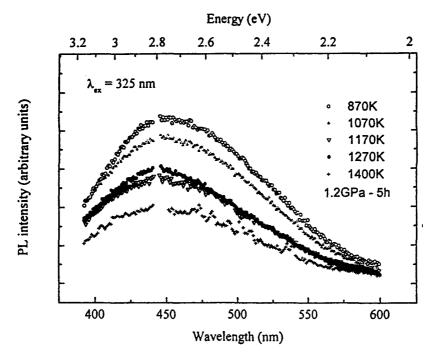


Figure 10. PL spectra from 120 nm thick Si<sub>3</sub>N<sub>4</sub>/Si samples treated at 870 - 1400 K - 1.2 GPa for 5 h.

The treatment of such samples at 1470 K - 1.5 GPa for 1 h resulted in much weaker PL (Fig. 9). A very broad PL band in the 400 - 550 nm region was observed for the  $Si_3N_4$  / Si samples treated at 870 - 1400 K - 1.2 GPa for 5 h ( $\lambda_{ex}$  = 325 nm). The intensity of this PL band diminished with increasing treatment temperature (Fig. 10). The intensity of PL in the 400 - 550 nm region did not depend much on pressure and time of treatment at 1470 K but practically disappeared for the  $Si_3N_4$  / Si samples treated at 1550 K - 1.5 GPa for 30' (Fig. 11).

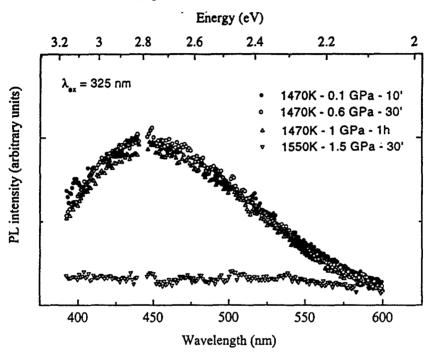


Figure 11. PL spectra from 120 nm thick  $Si_3N_4$ /Si samples after subjecting to HT - HP treatments at 1470 and 1550 K. PL excitation wavelength  $\lambda = 325$  nm.

### 4. Discussion

The HT - HP treatment effect (at up to 1550 K, 1.5 GPa, 10 h) on the photoluminescence properties of thin films (up to 1.2  $\mu$ m thickness) of SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub> and of silicon implanted silicon dioxide, SiO<sub>2</sub>: Si, on the single crystalline Cz-Si surface, is investigated in this work. All investigated films were prepared by oxidation of Cz-Si or by deposition of the respective material, so in fact the HT - HP effect on PL of the SiO<sub>2</sub>/Si, SiO<sub>2</sub>: Si/Si and Si<sub>3</sub>N<sub>4</sub>/Si systems was investigated.

Our results are "hot": they are the first obtained on the title subject. This paper contains mostly new results (only some of them were already published [5, 6,8]). In spite of performed investigations, many problems need further investigation and many questions remain to be answered. The presented discussion and conclusions are of preliminary character and demand deepening in future.

Most results were obtained on the  $\,$  HT - HP treated  $\rm SiO_2/Si$  and  $\rm SiO_2: Si/Si$  samples. They will be discussed jointly because, as it seems, the effects of HT - HP treatment are somewhat similar in both systems.

# 4. 1. PHOTOLUMINESCENCE FROM HT - HP TREATED SILICON DIOXIDE AND SILICON IMPLANTED SILICON DIOXIDE FILMS

To avoid, at least partially, problems with distinguishing real PL and the peaks from scattered radiation, we performed PL measurements using different excitation wavelengths (240, 250, 325 and 488 nm). One rather striking observation concerned lack of proportionality between the  $\mathrm{SiO}_2$  thickness and the PL signal intensity, which suggests that the "PL - related" HT - HP induced transformations in  $\mathrm{SiO}_2$  / Si are related to that at the  $\mathrm{SiO}_2$  / Si interface. Some PL results for the  $\mathrm{SiO}_2$  / Si samples are recapitulated (see also Figs 1 - 4) in the simplified form (only positions of PL peaks are presented, not accounting for their width and shape) in Table 1.

Table 1. PL peaks observed at RT from the  $SiO_2$  / Si samples subjected to specified HT - HP treatment. 290 nm thick  $SiO_2$  film was grown on Cz-Si wafer by annealing at 1470K in a wet oxygen ( $O_2 + H_2$ ) for 10 minutes.

HT - HP, K - GPa - time	Excitation wavelength, nm	PL peaks, nm 360 (?), 460(?)		
1170 - 1.2 - 5 h	240			
- ,, - ,, -	325		480	
1470 - 1.5 - 1 h	240	305, 340,	460(?)	
- ,, - ,, - ,, -	325		460	
1550 - 1.5 - 10'	240	305,	460	

The PL peak at 460 - 480 nm was detected for the HT - HP treated SiO<sub>s</sub>/Si samples (for excitation wavelength  $\lambda_{ex} = 325$  nm). In the case of excitation by 240 nm wavelength, this PL line seems to be superimposed on the scattered radiation peak. The 460 nm peak was shifted to higher energies for the samples treated at "severe" HT - HP conditions and disappeared after the 1550 K - 1.5 GPa - 2 h treatment (Fig. 3).

If using  $\lambda_{ex} = 240$  nm the peaks at 290 - 305 nm and 340 nm were detected for the samples treated at the highest temperatures and pressures (Figs 1, 2, Table 1), whereas the 360 nm PL peak (Fig. 10) was observed for the samples treated at lower temperature and pressures or for more short time.

The violet (at 432 nm) and yellow (at 561 nm) PL bands were reported for silicon dioxide thin films annealed by the RTA method [9]. PL at about 2.9 eV (430 nm) was detected for silicon oxide thin films prepared by dual plasma CVD [10]. This may be related to a defect associated with the OH groups. Radiation - induced PL from silica

reported for about 2.7 eV (460 nm), 3.1 eV (410 nm) and 4.3 eV (290 nm) is probably related to the presence of an "oxygen deficient center" (ODC) [11].

The PL band at 420 - 480 nm can originate from the nanocrystalline silicon formed in the SiO<sub>2</sub>/Si interface by thermal energy and thermal strain [9]. Other PL peaks can be related to some defects created in the SiO<sub>2</sub> film volume at HT - HP.

Photoluminescence spectra from the HT - HP treated  $SiO_2$ : Si samples are presented in Figs 5 - 8 and data are summarised for some samples in Table 2.

Table 2. PL peaks from the SiO<sub>2</sub>: Si/Si samples subjected to specified HT - HP treatment. 500 nm thick SiO<sub>2</sub> film on Cz-Si wafer was VHD - implanted with Si<sup>+</sup> ions.

HT - HP, K - GPa - time	Excitation wavelength, nm	PL peaks, nm				
720 - 0.01 - 10h	250	360,	460,	600	[5]	
- ,, - ,, - ,, -	488		650			
720 - 1.5 - 10h	250	360,	460,	600	[5]	
- ,, - ,, - ,, -	488		not observed			
720- 0.01-10 h + 1400K-1.2GPa	-5h 488	700				
720 - 1.5-10 h + 1400K-1.2GPa	-5h 488			6	80	

For the samples subjected to treatments at 720 K, the PL lines at 360, 460, 600 and 650 nm were detected (see also [5, 6]), whereas for that treated additionally at 1400K - 1.2 GPa - at 340 and 420 nm (for  $\lambda_{ex} = 250$  nm). A quite different PL band (at about 640 - 700 nm) was detected for such samples if excited by  $\lambda_{ex} = 488$  nm. This band is similar to that reported for the HT - HP treated bulk silicon samples [12].

An unique explanation of PL induced by HT - HP treatments in the  $SiO_2/Si$  and  $SiO_2:Si/Si$  samples is impossible at present. It is probable, however, that the origin of PL (especially at 460 nm) is the same for  $SiO_2/Si$  and  $SiO_2:Si/Si$  samples, and that the wide PL band at 460 nm is related to silicon nanoclusters created at the Si rich region of the  $SiO_2/Si$  interface in effect of pressure and thermally induced strains [9].

It is known that diffusivity of oxygen and probably of silicon decreases at HP [13] and that more small cluster - like defects are created at HT - HP, at least for the case of Si-O system [14]. This means that at HT - HP conditions, more silicon - related defects (possibly of the  $\equiv$ Si-Si $\equiv$  centres [5], "responsible" mainly for PL at 360 nm) will be created in the SiO<sub>2</sub>:Si film volume, whereas Si clusters ("responsible" for PL at 460 nm) would be created at the SiO<sub>2</sub>/Si and SiO<sub>2</sub>:Si/Si interfaces. Because of the mentioned diminished silicon diffusivity at HT - HP, the dimensions and concentration of the Si - related defects in the SiO<sub>2</sub>:Si thin film volume would be comparatively less dependent on the treatment temperature and time (but not on HP, because just HP results in larger concentration of such defects).

Such qualitative explanation accounts for ultraviolet / visible PL from the HT - HP treated  $SiO_2$  / Si samples (creation of Si nanoclusters at the Si rich regions of the  $SiO_2$  / Si interface [9]) and the shift of this PL line to higher wavelength with treatment time (related to the growth of dimensions of the Si nanoclusters created at the mentioned interface). The rise of PL intensity with HP in the  $SiO_2:Si/Si$  system can be related to stress stimulated creation of the  $SiS_0:Si$  centres in the  $SiO_2:Si/Si$  above explanation does not exclude, of course, other possible sources of HP - HT induced ultraviolet or visible PL: creation of "oxygen sufficient structures" [9] or of ODC [11].

# 4. 2. PHOTOLUMINESCENCE FROM HT - HP TREATED SILICON NITRIDE FILMS

As it follows from our rather preliminary investigations (Figs 9 - 11), the HT - HP treatment of the  $Si_3N_4/Si$  samples results in PL at about 290 and 360 nm (for excitation at  $\lambda_{ex}$  = 240 nm) or in the wide PL band peaking at about 450 nm (for excitation at  $\lambda_{ex}$  = 325 nm). The last is probably also present in the PL spectra obtained using  $\lambda_{ex}$  = 240 nm, but it is "hidden" because of the overlap with scattered radiation (Fig. 9). The intensity of PL at 450 nm decreases with treatment temperature at constant HP = 1.2 GPa (Fig. 10) and as a result of the treatment at 1550 K - 1.5 GPa - 30' (Fig. 11). The intensity of PL lines at 290 nm and 360 nm was the highest after the short time sample treatment at 1550 K (Fig. 9).

As prepared thin (120 nm)  $Si_3N_4/Si$  samples did not indicate measurable PL. For the thicker samples (300 nm) the wide PL band at 450 - 600 nm as well as comparatively narrow PL line at 390 nm and wide PL band at about 520 nm were reported (for excitation by  $\lambda_{ex} = 350$  nm) [7]. It seems that PL induced by the HT - HP treatment can be related (as in the case of discussed above  $SiO_2/Si$  and  $SiO_2:Si/Si$ ) to the stress stimulated creation of silicon nanoclusters at the  $Si_3N_4/Si$  interface.

#### 5. Conclusions

High pressure - high temperature treatment of SiO<sub>2</sub>, SiO<sub>2</sub>:Si and Si<sub>3</sub>N<sub>4</sub> thin films on single crystalline silicon surface results in the appearance of visible and ultraviolet photoluminescence, as well as in enhancement of photoluminescence intensity from the SiO<sub>2</sub>:Si samples containing silicon nanoclusters, in comparison to that from the samples subjected to similar processing but at atmospheric pressure. Further work in this field can help to reveal the physics of processes responsible for ultraviolet / visible PL in such systems and in improving of the existing technology.

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